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Synthesis, Characterization, and Crystal Structure of One Zinc(II) Complex with 4-Hydroxypyridine-2,6-Dicarboxylic Acid and 4,4'-bipyridine[1]

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Abstract—A new zinc(II) coordination polymer, $\{[Zn(HCAM)(4,4'\text{-}Bipy)_{0.5}] \cdot H_2O\}_n$ (**I**) (H_3CAM = 4-hydroxypyridine-2,6-dicarboxylic acid; 4,4'-Bipy = 4,4'-bipyridine), has been synthesized by hydrothermal reaction of $Zn(OAc)_2$, H_3CAM and 4,4'-Bipy. It has been structurally characterized by element analysis, IR-spectra. X-ray single-crystal analysis was carried out for **I** (CIF file CCDC no. 974199), which crystallizes in the orthorhombic system, space group *Pbca*. The single X-ray diffraction studies reveal that **I** shows a new 2D wave-like plane with 3-connected net. Furthermore, the thermal stability of compound **I** was studied.

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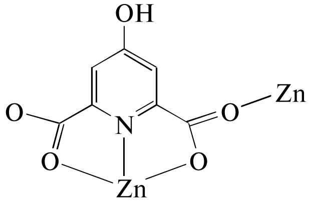
INTRODUCTION

Coordination polymers are of considerable interest due to their fascinating topology architectures and great variety of functional properties as promising candidates for special applications [1–5]. However, control-synthesizing coordination polymers and predicting their structures remain challenging. In fact, there are many factors in the formation of the structures, such as the choice of ligand, pH value, concentration, metal-to-ligand ratio, counterion and reaction temperature [6–11]. On the other hand, proper organic bridging linkers are critical in constructing coordination polymers. It is well known that carboxylate ligands play an important role to construct novel coordination polymers in coordination chemistry. They usually adopt various coordination modes after being deprotonated, such as terminal monodentate, chelating to one metal center, bridging didentate in a *syn-syn, syn-anti*, and *anti-anti* configuration to two metal centers, and bridging tridentate to two metal centers [12–14]. A large number of coordination polymers containing carboxylate ligands have been prepared, and most of them are unique structures and topologies [15, 16].

Actually, in the construction of coordination polymers, it is well known that organic ligands play an important role, especially pyridine-carboxyl ligands were widely employed. 4-hydroxypyridine-2,6-dicarboxylic acid (H_3CAM) as a very important carboxylate derivative has attracted much interest in coordination chemistry. It has a rigid 120° angle between the pyridine ring and two carboxylate groups. Therefore, it could potentially provide various coordination motifs to form both discrete and consecutive metal complexes under suitable synthesis condition. A systematic study of 4*f*, 3*d*–4*f* and 4*d*–4*f* complexes based on H_3CAM has been undertaken in P. Cheng lab [17–20].

In this paper, we select H_3CAM and Zn salt and employed hydrothermal synthesis to get a new 2D coordination polymer, $\{[Zn(HCAM)(4,4'\text{-}Bipy)_{0.5}] \cdot H_2O\}_n$ (**I**). At the same time, the thermal stability of compound **I** was studied. Coordination mode of the H_3CAM ligand in compound **I** is shown in Scheme 1:



Scheme 1.

EXPERIMENTAL

Reagents and physical measurement. All reagents were of analytical grade and were used without further purification. Elemental analyses for carbon, hydrogen and nitrogen atoms were carried out on a Vario EL III elemental analyzer. The infrared spectrum of a KBr pellet was recorded in the range of 4000–600 cm^{-1} on an Avatar^{TM} 360 E.S.P. IR spectrometer. The thermogravimetric analyses (TGA) were performed on a SII Exstar6000 TG/DTA6300 integration thermal analyzer in flowing N2 with a heating rate of 10°C min^{-1}.

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for **I**

Parameter	Value
Formula weight	342.58
Temperature, K	296(2)
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions:	
a, Å	18.763(2)
b, Å	7.1628(8)
c, Å	18.966(2)
Volume, Å^3; Z	2548.9(5); 8
ρ_{calcd}, mg/m^3	1.785
Absorption coefficient, mm^{-1}	1.958
F(000)	1384
Crystal size, mm	0.46 × 0.15 × 0.13
θ Range for data collection, deg	2.41–25.50
Limiting indices	$-22 \le h \le 22$, $-8 \le k \le 8$, $-22 \le l \le 22$
Reflections collected	18073
Independent reflection (R_{int})	2381 (0.0353)
Parameters	191
Goodness-of-fit on F^2	1.005
Final R indices, $I > 2\sigma$, I	$R_1 = 0.0260$, $wR_2 = 0.0662$
R indices, all data	$R_1 = 0.0342$, $wR_2 = 0.0712$
Largest diff. peak and hole, e/Å^3	0.284 and –0.283

Synthesis of I. A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.10 mmol, 22 mg), H_3CAM (0.20 mmol, 37 mg), and 4,4'-Bipy (0.10 mmol, 16 mg) was successively dissolved in deionized H_2O (10 mL). The mixture was transferred into a 25 mL Teflon-lined stainless steel vessel and heated at 150°C for 3 days under autogenous pressure and then cooled slowly to the room temperature. The colourless blocked crystals were recovered after washing with deionized water and ethanol, and allowed to dry in air. The yield was 54% (based on Zn^{2+}).

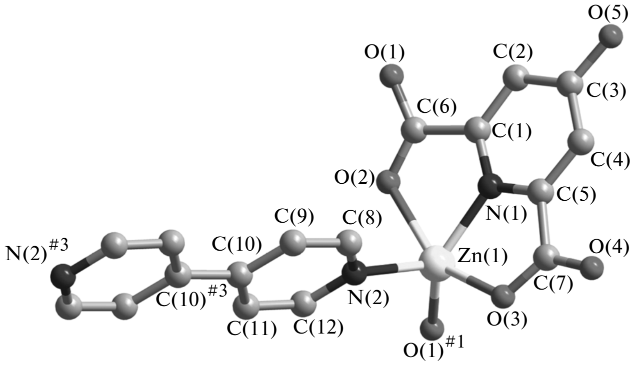

Fig. 1. Coordination environment of Zn atom in **I** (symmetry codes: $^{\#1}$ $-x, y + 1/2, -z + 1/2$; $^{\#3}$ $-x, -y, -z$).

For $C_{12}H_9N_2O_6Zn$

anal. calcd., %:	C, 42.07;	H, 2.65;	N, 8.18.
Found, %:	C, 41.89;	H, 2.72;	N, 8.11.

IR spectrum (KB; ν, cm^{-1}): 3605 w, 3245 w, 1612 s, 1571 s, 1505 w, 1466 w, 1432 w,1375 m, 1353 s, 1308 w, 1243 m, 1022 m, 1012 w, 945 w, 868 w, 779 m, 727 m.

Crystal structure determination. Colourless single crystal of **I** with dimensions of 0.46 × 0.15 × 0.13 mm was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by using ϕ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97 [21]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [22]. The final agreement factor values are $R = 0.0260$ and $wR = 0.0662$, $w = 1/[\sigma^2(F_o)^2 + (0.0381P)^2 + 1.6328P]$, where $P = (F_o^2 + 2F_c^2)/3)$, $S = 1.005$, $(\Delta/\sigma)_{max} = 0.001$. $(\Delta\rho)_{max} = 0.284$ and $(\Delta\rho)_{mix} = -0.283$ e/Å^3. The crystallographic details of I are summarized in Table 1. Selected bond lengths and angles for **I** are collected in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 974199; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The crystal structure of complex **I** is shown in Fig. 1. X-ray single crystal diffraction analysis reveals that crystallizes in *Pbca* space group and exhibits a 2D layered framework. The asymmetric unit consists of one Zn^{2+} ion, one $HCAM^{2-}$ ligand, half of 4,4'-Bipy ligand and one attice water. Each Zn^{2+} ion is five-coordinated, its coordination sphere is defined by one Bipy N atom, one pyridine N atom and three corboxylate O atoms. Zn(1) has a distorted ZnO_3N_2 square-pyramidal coordination environment (τ = 0.26). The basal plane contains a chelating $HCAM^{2-}$ ligand carboxylate group and pyridine nitrogen (O(2), O(3), N(1)) and a single oxygen donor from another $HCAM^{2-}$ ligand carboxylate group (O(1)$^{\#}$); the apical site contains a Bipy nitrogen donor atom (N(2)). The Zn–O bond lengths are 1.9490(16), 2.3307(17) and 2.1287(16) Å, and two Zn–N bond lengths are 2.0025(18) and 2.0236(19) Å, respectively. The coor-

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Zn(1)–O(1)$^{\#1}$	1.9490(16)	Zn(1)–O(3)	2.1287(16)
Zn(1)–N(1)	2.0025(18)	Zn(1)–O(2)	2.3307(17)
Zn(1)–N(2)	2.0236(19)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)$^{\#1}$Zn(1)N(1)	135.66(7)	O(3)Zn(1)O(2)	151.35(6)
O(1)$^{\#1}$Zn(1)N(2)	104.90(7)	C(1)N(1)Zn(1)	122.52(14)
N(1)Zn(1)N(2)	117.95(8)	C(5)N(1)Zn(1)	117.45(15)
O(1)$^{\#1}$Zn(1)O(3)	106.90(7)	C(8)N(2)Zn(1)	119.21(16)
N(1)Zn(1)O(3)	78.08(7)	C(12)N(2)Zn(1)	123.67(16)
N(2)Zn(1)O(3)	99.34(7)	C(6)O(1)Zn(1)$^{\#2}$	113.87(15)
O(1)$^{\#1}$Zn(1)O(2)	97.58(7)	C(6)O(2)Zn(1)	111.83(14)
N(1)Zn(1)O(2)	74.01(6)	N(2)Zn(1)O(2)	88.24(7)

* Symmetry codes: $^{\#1}$ $-x, y + 1/2, -z + 1/2$; $^{\#2}$ $-x, y - 1/2, -z + 1/2$.

Table 3. Geometric parameters of hydrogen bonds for **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(5)–H(5)···O(6)	0.82	1.80	2.610(3)	170
O(6)–H(1w)···O(4)$^{\#4}$	0.82	1.96	2.744(3)	160
O(6)–H(2w)···O(4)$^{\#5}$	0.82	2.43	3.124(3)	143
O(6)–H(2w)···O(3)$^{\#5}$	0.82	2.63	3.177(3)	125

* Symmetry codes: $^{\#4}$ $x, -y + 3/2, z + 1/2$; $^{\#5}$ $-x + 1/2, -y + 1, z + 1/2$.

dination angles around the Zn(1) are in the range of 78.08(7)°–151.35(6)°, which are all in great agreement with the reported lengths [23, 24].

Each $HCAM^{2-}$ molecule by three tridentate (ONO) chelates to one Zn^{2+} ion and links to one Zn^{2+} ion. Notably, the $HCAM^{2-}$ ligand acts as a μ_2-bridge using its two carboxylate groups with μ_2-O,N,O mode (Scheme 1) due to its preferential and stable chelated configuration, and connects Zn(II) atoms to form an infinite one-dimensional $[Zn(HCAM)]_n$ chain (Fig. 2). The neighboring Zn^{2+} ions in 1D chain are separated with Zn(1)···Zn(1) distance of 5.144 Å. Then, the 1D chains are further linked together by 4,4'-Bipy ligand to generate a two-dimensional (2D)

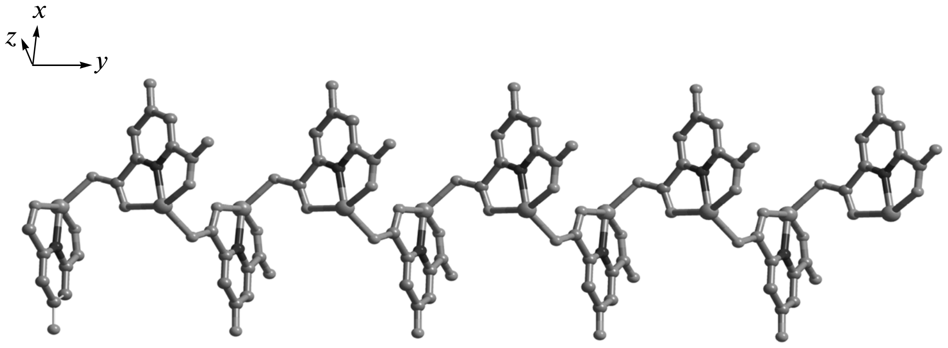

Fig. 2. View of one section of the 1D $[Zn(HCAM)]_n$ chain of **I**.

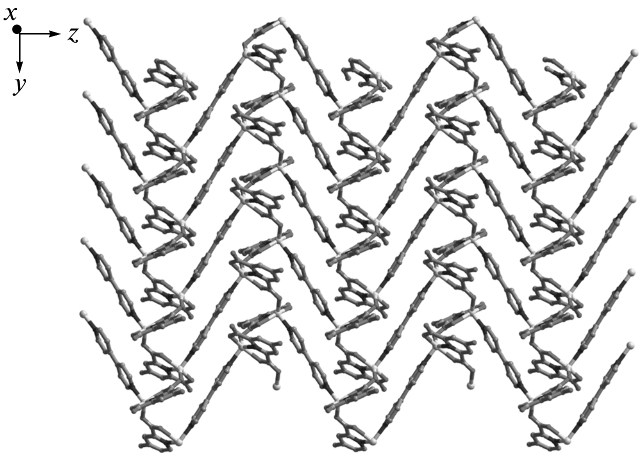

Fig. 3. View of the 2D wave-like layer of **I** in *yz* plane.

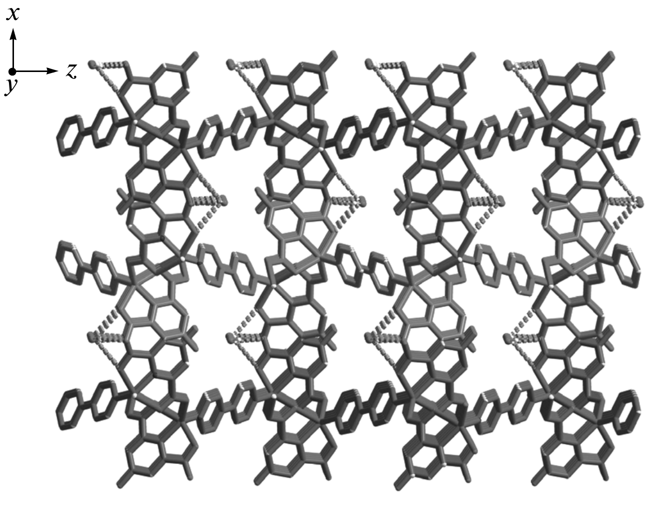

Fig. 5. 3D supramolecular architecture in **I**.

wave-like network (Fig. 3). From topological view, the center of the Zn atom acts as node to link each other through $HCAM^{2-}$ and 4,4'-Bipy ligands into a 3-connected 2D network with a Schläfli symbol (6^3) topology (Fig. 4) uninodal net. It should be noted that the oxygen atom from hydroxyl group of $HCAM^{2-}$ ligand do not coordinate to any metal atom, which direct the formation of hydrogen bonds with water molecules. The hydrogen bonds (O(5)–H(5)···O(6), O(6)–H(1*w*)···$O(4)^{\#4}$, O(6)–H(2*w*)···$O(4)^{\#5}$ and O(6)–H(2*w*)···$O(3)^{\#5}$ (symmetry codes: $^{\#4}$ $x, -y + 3/2, z + 1/2$; $^{\#5}$ $-x + 1/2, -y + 1, z + 1/2$) (Table 3) between carboxylate O atoms or OH groups and water molecules link the 2D coordination sheets to form a 3D supramolecular structure (Fig. 5).

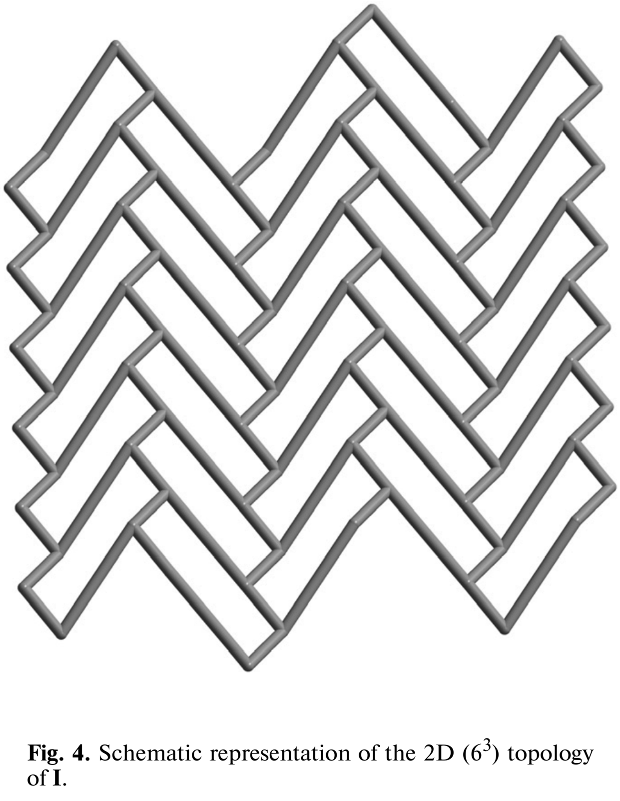

Fig. 4. Schematic representation of the 2D (6^3) topology of **I**.

To further fully characterize the title compound, its thermal stability was examined using TG-method. TG curve has been obtained in N_2 atmosphere for crystalline samples of the title compound in the temperature range of 30–900°C. TG curve of the title compound exhibits two main steps of weight loss. The first one occurs from 80 to 175°C, which can be attributed to the release of crystallization water molecule per formula unit. The observed weight loss of 5.16% is in good agreement with the calculated value (5.26%). The further weight loss of I between 290 and 900°C may attribute to the partly decomposition of the ligands.

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